

# **ORGANIC CHEM**

## **10.5 –**

### **HALOGENALKANES**

### **SN1 & SN2 REACTIONS**

IB Chemistry

Topic 10 – Organic





# 10.5 – Halogenalkanes – 2hrs

- 10.5.1 Describe, using equations, the substitution reactions of halogenoalkanes with sodium hydroxide. (2)
- 10.5.2 Explain the substitution reactions of halogenoalkanes with sodium hydroxide in terms of SN1 and SN2 mechanisms. (3)





# 10.5 Halogenalkanes

- Halogenalkanes contain an atom of fluorine, chlorine, bromine, or iodine bonded to the carbon skeleton of the molecule
- General formula  $C_nH_{2n+1}X$ , where  $X$ =halogen
- Generally oily liquids that do NOT mix with water
- Saturated compounds in which the halogen can be replaced by other atoms or groups in **substitution reactions**.



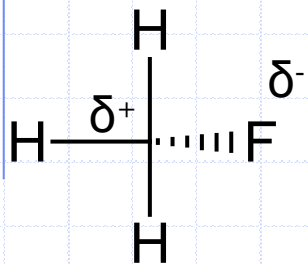
◆ Ex. CFC's common in aerosols, break down ozone layer



# Equations of Substitution of Haloalkanes

10.5.1 Describe, using equations, the substitution reactions of halogenoalkanes with sodium hydroxide. (2)

- For halogenalkanes, the greater electronegativity of the halogen atom means that the C-H bond is polarized



- The Central Carbon has a partial positive charge making it electron deficient and makes it susceptible to attack by nucleophiles (nucleus seeking) species

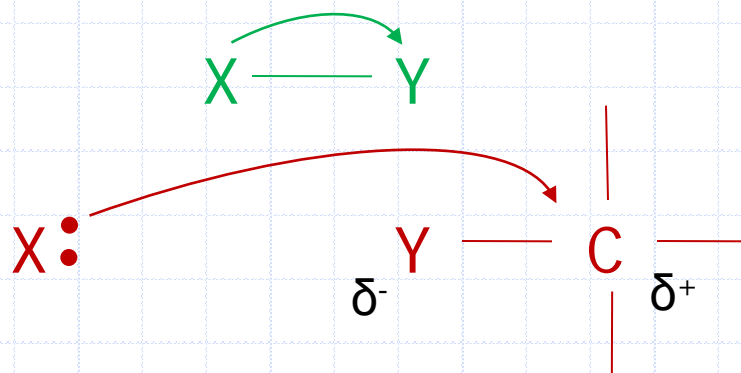
- Halogenalkanes are saturated compounds, so **substitution** reactions are the most common
  - Substitution of **hydroxide ( $\text{OH}^-$ )** containing compounds is common and are known as  **$\text{S}_\text{N}$**  for **nucleophilic substitution**





# Convention for depicting organic reaction mechanisms

- Showing movement of electrons
  - Within bonds and between reactants
- The curly arrow is used
  - Drawn from the site electron availability to the site of electron deficiency.



Represents e<sup>-</sup> pair being pulled towards Y so Y becomes  $\delta^-$  and X becomes  $\delta^+$

Nucleophile X attracted to e-deficient C

The double-headed arrow represents the motion of an electron pair. When electrons are fully transferred through several steps they are known as the "leaving group."





# **$S_N1$ & $S_N2$ Reaction Mechanisms:**

10.5.2 Explain the substitution reactions of halogenoalkanes with sodium hydroxide in terms of  $S_N1$  and  $S_N2$  mechanisms. (3)

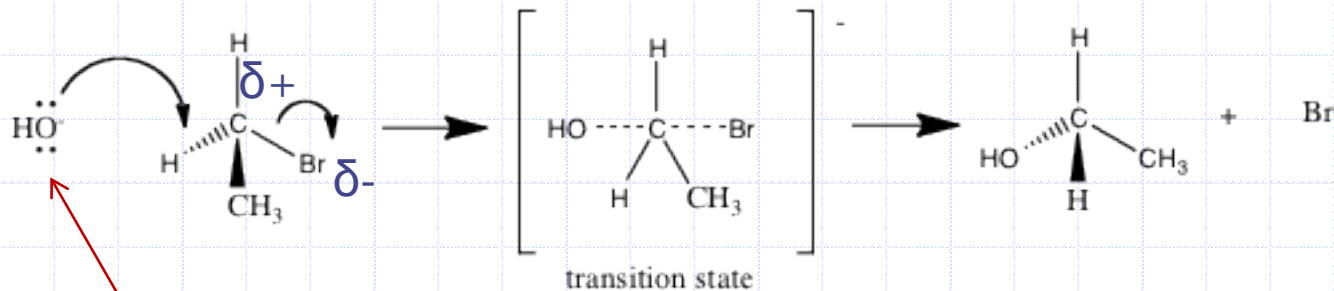
- **Primary halogenoalkanes** = single step
  - One-stage reaction involves the simultaneous attack of the nucleophile and departure of the halide (leaving group)
  - **$S_N2$**  – Nucleophilic Substitution Bimolecular
- **Secondary halogenoalkanes** = dependent
  - A mix of  $S_N1$  and  $S_N2$  reactions
- **Tertiary halogenoalkanes** = two steps
  - Due to **steric hindrance** a stable intermediate (tertiary cation) must be formed before the nucleophile can attack
  - **$S_N1$**  – Nucleophilic Substitution Unimolecular





# Primary Halogenalkane Substitution $S_N2$

- Simultaneous attack of nucleophile and departure of leaving group
- $\text{CH}_3\text{CH}_2\text{Br}(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{CH}_3\text{CH}_2\text{OH}(\text{aq}) + \text{Br}^-(\text{aq})$ 
  - Single Step Reaction involving both [bromoethane] &  $[\text{OH}^-]$
  - Rate =  $k[\text{CH}_3\text{CH}_2\text{Br}(\text{aq})][\text{OH}^-(\text{aq})]$
  - 2<sup>nd</sup> Order, therefore  $S_N2$  (bimolecular)
  - There is a transition state but not a stable intermediate

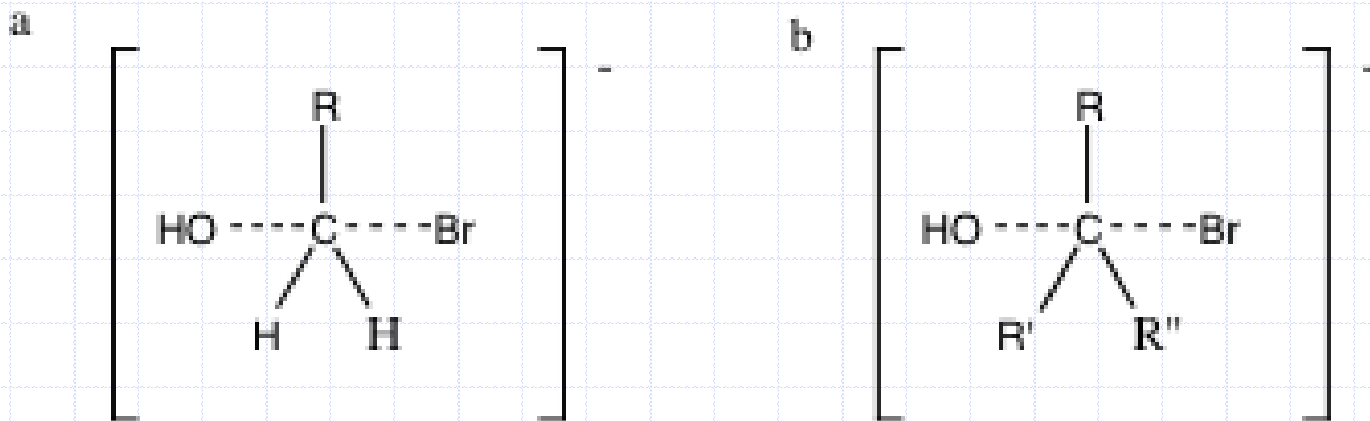


nucleophile



# Steric Hindrance in Secondary and Tertiary Halogenalkanes

- When comparing the extremes, primary (a) and tertiary (b) halogenalkanes the bulkiness of the compounds can be demonstrated:



- Where the R' and R'' groups are bulky extensions of the hydrocarbon chain that will not allow for the simultaneous attack of the nucleophile and departure of the leaving group.

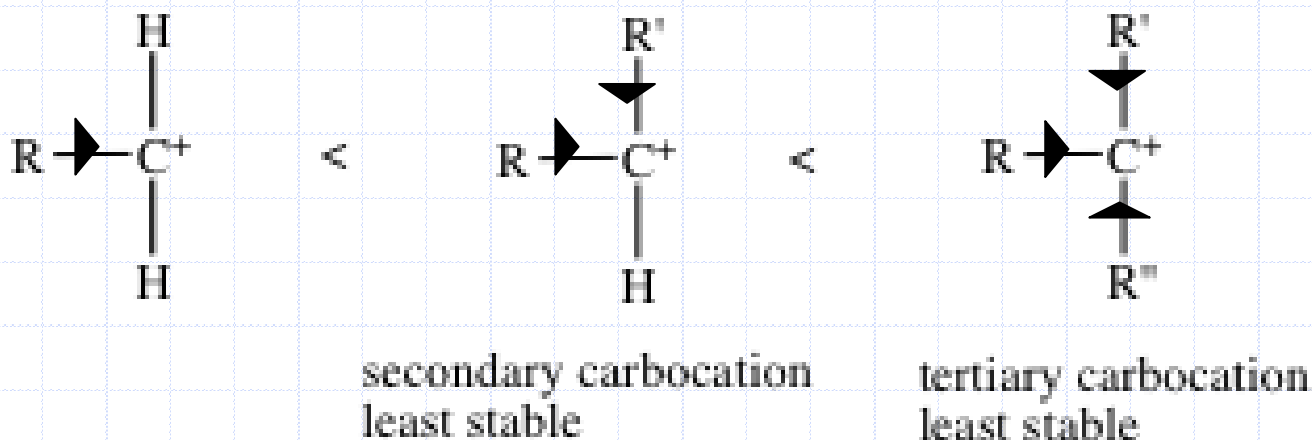


A new mechanism is needed: S<sub>N</sub>1



# Stability of Cations

- The stability of a tertiary cation allows for the mechanism of tertiary halogenalkane substitution to form an intermediate



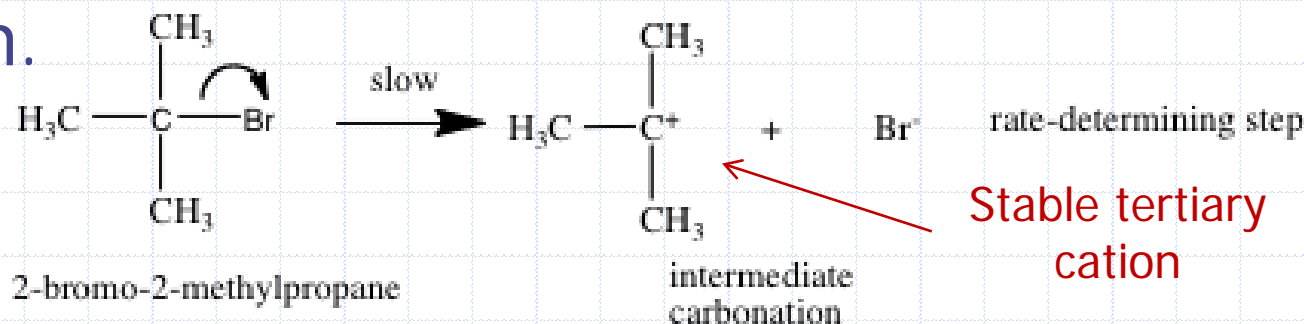
- The tertiary cation is stabilized by three alkyl groups which are electron-donating (demonstrated by the arrows above)





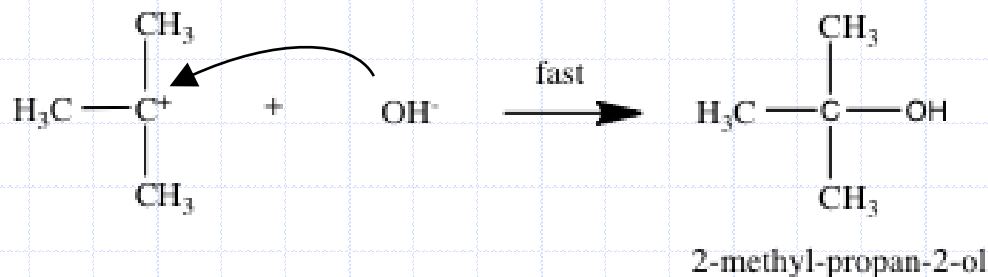
# Tertiary Halogenalkane Substitution S<sub>N</sub>1

- $\text{CH}_3\text{C}(\text{CH}_3)_2\text{Br}(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{CH}_3\text{C}(\text{CH}_3)_2\text{OH}(\text{aq}) + \text{Br}^-(\text{aq})$
- Kinetic Studies show this as a multi-step reaction with the rate determining step being the 1<sup>st</sup> step
  - The departure of the halogen to form a stable tertiary cation.



■ Rate =  $k[\text{CH}_3\text{C}(\text{CH}_3)_2\text{Br}(\text{aq})]$  1<sup>st</sup> order = S<sub>N</sub>1

■ 2<sup>nd</sup> step is fast:





# Reactivity of Halogenalkanes

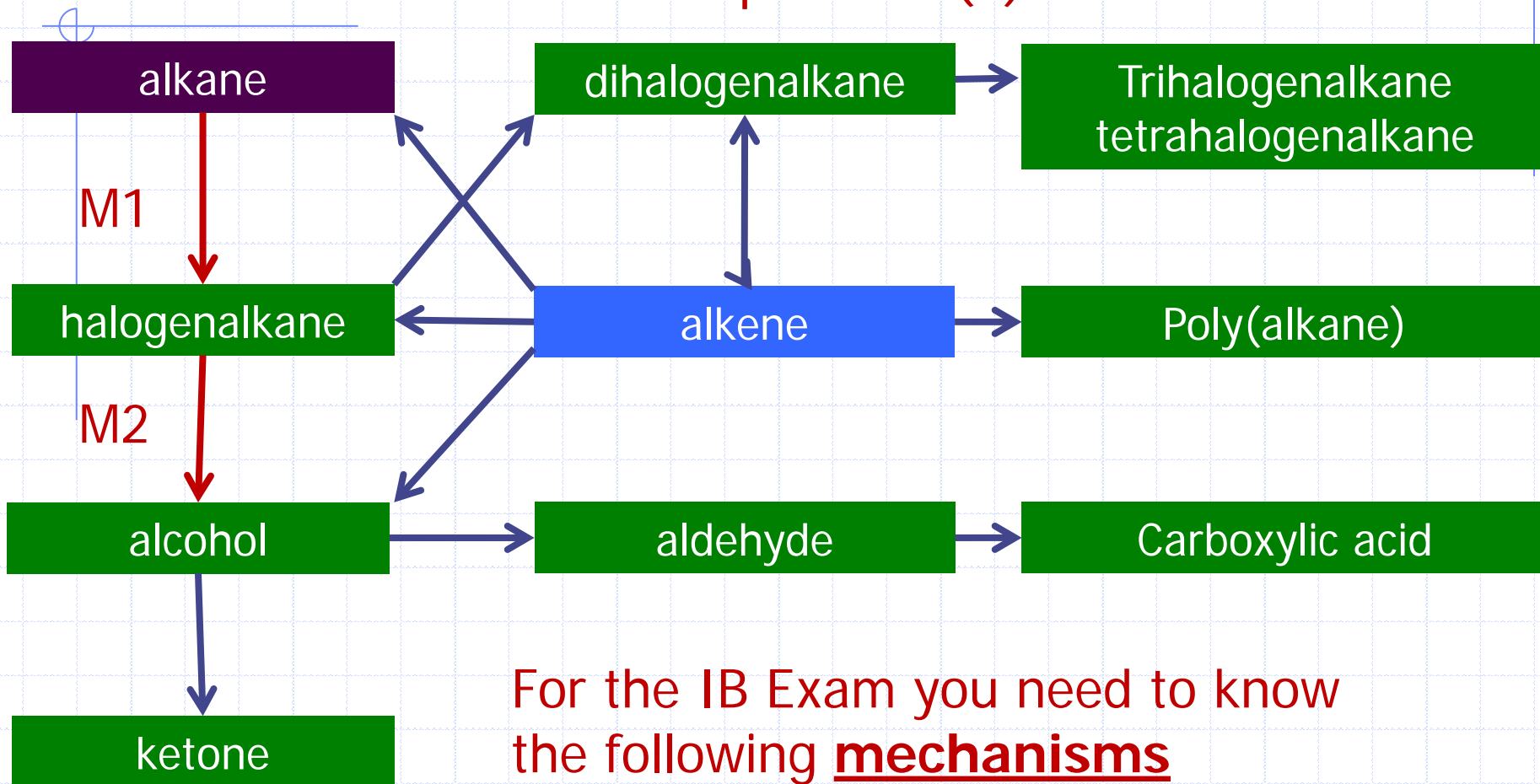
- The reactivity is dependent on the strength of their bonds with the carbon backbone
  - Bond strength decreases down a group
    - ◆ Due to increased electron shielding effect relative to increased nuclear charge
    - ◆ Iodoalkane (longest, weakest bond) is the most reactive
    - ◆ Fluoroalkane (shortest, strongest bond) is the least reactive





# Reaction Pathways

10.6.1 Deduce reaction pathways given the starting materials and the product. (3)



For the IB Exam you need to know the following mechanisms

**M1 – Halogen / UV light**

**M2 – NaOH**

